

ALUMINUM ASSOCIATED WITH A PH-INCREASE IN THE HUMUS LAYER OF A BOREAL HAPLIC PODZOL

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Aluminum (Al) is generally considered to be a major problem for the vitality and productivity of acid tropical and temperate forest soils. It is the soluble inorganic Al species that seem to affect the morphology and functioning of roots. The chemical processes involving Al-compounds in the solid phase, in the soil solution phase or on the soil adsorption complex are also coupled to a consumption or production of protons.

In the spodic horizon of podzols the amount of soluble Al is regulated by the solubilization of Al-silicates and Al-hydroxides. Although a substantial amount of soluble Al occurs as organo-metallic complexes (e.g. Cronan and Schofield, 1979; David and Driscoll, 1984), a negative correlation is often found between pH and Al in the soil solution of spodic horizons (Reuss *et al.*, 1990; Berggren, 1992). If the reference-pH for the acid neutralization capacity of the soil is set to 4.5 ($ANC_{pH\ 4.5}$) or higher, Al^{3+} is considered to be an acid cation, owing to its release of protons upon hydrolyzation.

In organic horizons the relationship between pH and soluble Al is more puzzling. Soil solution has been found to be highly undersaturated for dissolved Al in relation to pH and possible Al-hydroxides or Al-silicates (David and Driscoll, 1984; Nätcher, 1987). Laboratory experiments have shown this to be caused by an equilibrium between soluble

Al and Al bound to soil organic matter (Bloom *et al.*, 1979; Hargrove and Thomas, 1982; Cronan *et al.*, 1986).

Several artificial acidification experiments have shown that cation exchange between H^+ and alkali and alkali-earth cations is the basic pH-buffering process in naturally acid organic horizons (James and Riha, 1986; Brown, 1987; Kreutzer *et al.*, 1989; Nätcher and Schwertmann, 1991; Vance and David, 1991). The degree of exchange between Al and H^+ seems to vary between O-horizons, and has been found to be important in soils with substantial amounts of exchangeable Al (Nätcher and Schwertmann, 1991). Exchange reactions between Al-cations and H^+ on organic matter exchange sites has in laboratory experiments been shown to be an important source of pH-buffering in acid topsoils (Bloom *et al.*, 1979; Walker *et al.*, 1990). Furthermore laboratory experiments have shown that organic matter saturated with Al gives a higher pH in soil suspension compared with organic matter saturated with H^+ , owing to the lower acid strength of Al-organic matter (Hargrove and Thomas, 1982; Nätcher and Schwertmann, 1991).

Soil chemistry studies often include different soil types or soils from different areas in order to obtain variation in the factors studied. Results from such studies are difficult to interpret in terms of chemical processes owing to variation in factors that probably should

have been kept fixed. To minimize the unwanted variation associated with large-scale factors the experimental area can be reduced.

The objectives of this study were to examine the influence of exchangeable Al on the small-scale variability of pH_{CaCl_2} , pH_{H_2O} and exchangeable protons in sliced one-cm-layers of the O-horizon (mor layer). An intensive soil sampling was undertaken within small plots (1 to 100 m²) in a *Picea abies* (L.) Karst stand, to minimize the influence of larger-scale factors.

Material and methods

Sampling and sample treatment

The soil was sampled from four plots of different sizes: plot A, 100 m² (10 by 10 m); plots B and C, 4 m² (2 by 2 m); plot D, 1 m² (1 by 1 m). The B and C plots were randomly placed within the A plot, which represented the experimental stand (Table I), and plot D was randomly placed in one quadrant of plot C. Thirteen sampling points were selected in a systematic grid in each of the plots A, B and C, and eight were selected in plot D, giving a total of 47 sampling points.

Two humus cores and two cores from the E-horizon, each with a 70 mm diam., were taken at every sampling point, sliced into one-cm-layers (Skylberg, 1990) and mixed to give one

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sample per cm-layer and sampling point. In plot A the mineral soil was also sampled at depths of 10 to 15, 20 to 25 and 50 to 55cm in the upper and lower Bs- and B/C-horizons, respectively. All samples were taken from 28 June to 1 July 1988, and were immediately frozen until analyzed. Mineral soils were manually homogenized and particles larger than 2mm manually separated before analyses.

Analyses

pH_{H_2O} , pH_{CaCl_2} , exchangeable aluminum (Al_e) and exchangeable protons (H_e)

The deep-frozen soil samples were thawed at room temperature overnight. Moist samples were used for all analyses to avoid chemical changes upon drying (Bartlett and James, 1980). Due to variation in the water contents of the moist samples, measured pH-values and KCl-extracted hydrogen ions were corrected with a nonlinear function to obtain corresponding data for a constant extraction solution:soil mass ratio (Skjellberg, 1991; Skjellberg, 1993). This is important, especially in organic horizons where pH is strongly buffered by organic acids. To be able to express hydrogen ions in relation to ash-free organic matter (loss on ignition, LOI), a similar correction was undertaken. Exchangeable cations other than hydrogen ions were, however, linearly corrected for water contents and LOI (Skjellberg, 1993).

A mass of 3.0g moist humus or 10.0g moist mineral soil was suspended in 30ml of 0.01M $CaCl_2$. After four hours of shaking followed by one hour of sedimentation, the pH_{CaCl_2} (abbreviated pH_C) was measured. The pH_{H_2O} (abbreviated pH_H) was measured in the similar way, but in distilled water. The values were corrected to correspond to a solution:soil mass ratio of 30:1 in humus and 4:1 in mineral soil.

Effective exchangeable acidity ($H_e + Al_e$) was obtained by extracting 3.0 g moist humus or 10.0g moist mineral soil in 25ml of 1.0M KCl for 30 min. The humus suspensions were filtrated through a Munktell analytical filter paper no. 3, and the mineral soil suspensions were filtrated through paper 00H. The soil was additionally washed with 125ml 1.0M KCl. The filtrate was titrated with NaOH to pH 8.2. Thus the reference pH for acidity was set to 8.2. The acidity was separated into Al_e and H_e by adding 10ml 1M KF and back-titrating according to Thomas (1982). The method does not distinguish between Al

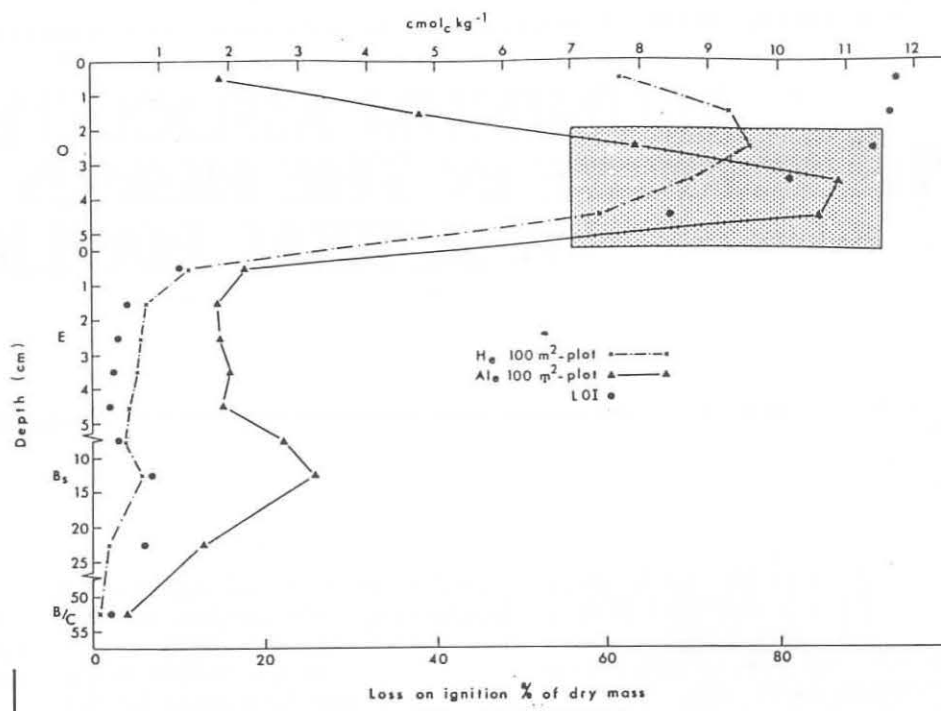


Figure 1. Mean values of exchangeable hydrogen ions (H_e), exchangeable aluminum (Al_e) and loss on ignition (LOI) from plot A (100 m², n=13). Note that 0-levels for the O-horizon and the mineral soil differ. This paper is mainly concerned with interactions between H and Al in the stippled part of the profile.

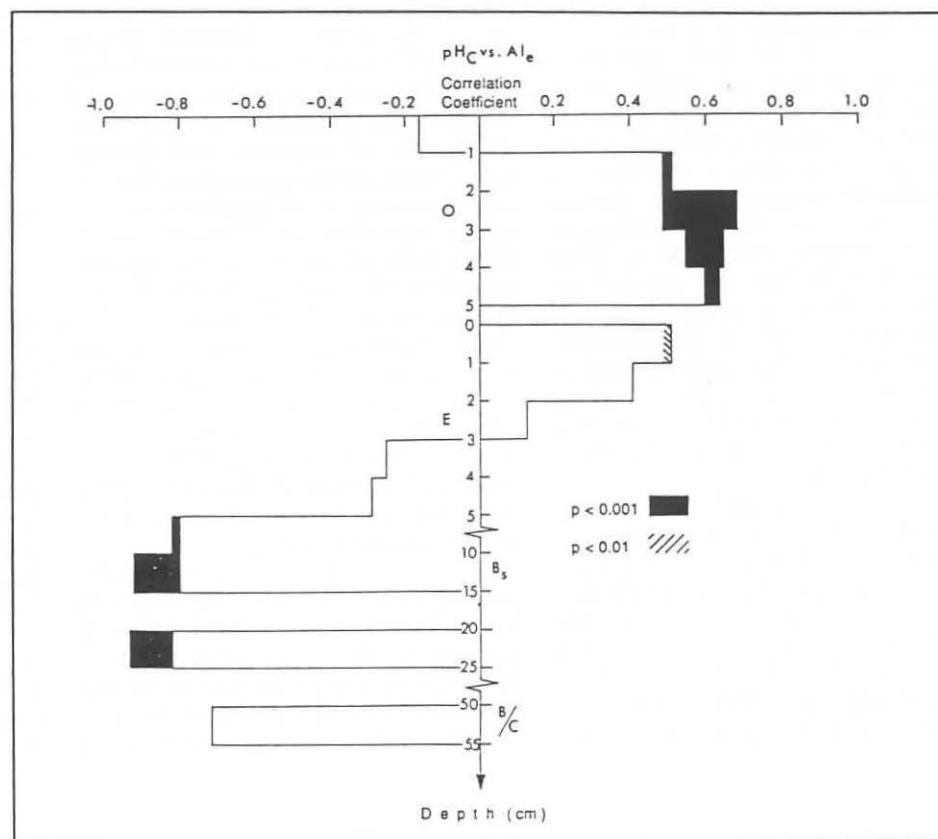


Figure 2. Simple linear correlation coefficients between pH_C and Al_e at different depths in the Haplic Podzol profile. The hatched areas of the bars illustrate the degree of significance. The degree of significance varied with depth depending on the number of samples (n=27-32 in the O-horizon and n=13 in the mineral soil horizons). Note that 0-levels for the O-horizon and the mineral soil differ.

and Fe and therefore Al_e -values contain small amounts of exchangeable Fe. The titrations were performed automatically to a given pH on a Mettler DL 70 titrator. The corrected H_e corresponded to a total extraction solution:soil mass ratio of 150:1 in humus and 20:1 in mineral soil and was, as well as Al_e , expressed as centimoles of charge per kilogram dry soil ($cmol_c kg^{-1}$).

Effective cation exchange capacity (CEC_e)

Exchangeable Ca, Mg, K, Na and Mn were obtained by extracting 3.0 g moist humus for two hours in 30 ml of 0.5 M $CuCl_2$, followed by filtration through a Munktell analytical filter paper no. 3. The soil was washed with another 30 ml of $CuCl_2$ solution before an elemental analysis of the filtrate was made on a Perkin-Elmer ICP-AES instrument. Nätscher (1987) found a good 1:1 correspondence between the amounts of Ca, Mg, K, Na and Mn obtained in 0.33 M $CuCl_2$ and the amounts obtained in 1.0 M NH_4Cl in mor layers. Total amounts of organically bound Al (Al_{cu}) and Fe (Fe_{cu}) were also determined in the above mentioned $CuCl_2$ filtrates (Juo and Kamprath, 1979; Hargrove and Thomas, 1984). The effective cation exchange capacity (CEC_e) was calculated as $cmol_c kg^{-1}$ $(Ca+Mg+K+Na+Mn)_{CuCl_2} + (H+Al)_{KCl}$ and the effective base saturation ($V_e\%$) as $100(Ca+Mg+K+Na)/CEC_e$.

Table II presents chemical properties of the experimental site, expressed on an areal basis ($kmol_c ha^{-1}$). Total acidity (TA) was titrated up to pH 8.2 in accordance with Thomas (1982). The loss on ignition (LOI) was expressed in relation to dry mass. The samples were combusted 4-6 h at 500° C until no traces of carbon were left.

Estimation of the acid strength of humus samples

Mixed humus samples were formed to represent each of the five cm-layers from plot B. For each of the 0-1 cm and 4-5 cm-layers only one mixed sample was formed, whereas two mixed samples with different amounts of Al_e were formed for each of the 1-2, 2-3 and 3-4 cm-layers. Five grams of each mixed sample was H⁺-saturated by shaking it in 50 ml of 1.2 M HCl for 24 h, before centrifugation at 13000 rpm for 10 min. The centrifuged soil was washed twice with 50 ml distilled water, with each washing followed by centrifugation at 13000 rpm. Washings with 100 ml distilled water were alternated with suction

TABLE I
DESCRIPTION OF THE EXPERIMENTAL SITE AND THE SOIL STUDIED AT KULBÄCKSLIDENS
FÖRSÖKSPARK IN NORTHERN SWEDEN

Location	64 10' N lat, 19 35' O long, 285 m alt.		
Mean annual temperature (1931-1960)	annual 1.3 C	Mean annual precipitation (Hällnäs 1931-1960)	annual 533 mm
Vegetation	January -11.8 C	July 15.4 C	
	tree layer	135-year-old <i>Picea abies</i>	
	field layer	dwarf shrub, <i>Vaccinium myrtillus</i> scattered grass, <i>Deschampsia flexuosa</i>	
	bottom layer	<i>Pleurozium schreberi</i> <i>Hylocomnium splendens</i>	
Parent material	glacial till originating from predominantly gneissic bedrock.		
Soil texture fractions <2mm	2.0-0.05 mm	54%	
	0.05-0.02 mm	20%	
	0.02-0.002 mm	21%	
	<0.002 mm	5%	
Soil classification	Haplic Podzol according to the FAO system (FAO, 1988). Typic Cryorthod according to Soil taxonomy (Soil Survey Staff, 1990).		
O-horizon	A typical mor layer consisting of L (S), F and H subhorizons (thickness in parentheses): L (2-3 cm) - Better classified as an S-layer (Forsslund, 1943), with living mosses and litter mixed together; a decomposition zone with hyphae demarcates the border between the S- and F-layers; abrupt, smooth boundary. F (1-3 cm) - Slightly decomposed residues from mosses and needles interwoven with fine roots and hyphae, giving a mat-like structure; fibrous; gradual, wavy boundary. H (1-4 cm) - Predominantly strongly decomposed organic matter; some samples were black, greasy, massive structureless, others were dark brown with fine structure; many fine roots; rhizomes from <i>Vaccinium myrtillus</i> abundant within the abrupt, wavy boundary.		
Ah-horizon	0.5-1.5 cm thick		
E-horizon	0-8.5 cm depth, color: light grey (10 YR 7/1, dry)		
Bs-horizon	8.5-35 cm depth, color: light olive brown (2.5 Y 5/6, dry)		

TABLE II
SOME CHEMICAL PROPERTIES (N=13) AND THE BULK DENSITY (BD, N=6-13) OF THE HAPLIC PODZOL PROFILE, FROM PLOT A. THE CEC_e-VALUES OF THE O-HORIZON WERE TAKEN FROM PLOT B (N=13) AND THE CEC_e-VALUES OF THE MINERAL SOIL HORIZONS WERE TAKEN FROM PLOT A (MIXED SAMPLES)

Horizon	pH _{CaCl2}	H _e	Al _e	CEC _e	TA	V _e	LOI	BD
			----- $kmol_c ha^{-1}$ -----			---- % ----		$mg m^{-3}$
O 0-1 cm	3.40	6.8	5.6	27.6 27.6	102	55 38	83.6	0.15
CV%	3.2	18	68	11	12		6.0	15
E 0-5 cm	3.73	3.5	8.7	14.8	40	18	5.5	0.90
CV%	3.2	25	38		24		33	13
Bs 10-15 cm	4.29	3.4	15.4	20.6	133	9	6.7	0.96
CV%	4.4	56	33		32		35	29
Bs 20-25 cm	4.62	0.8	6.6	7.8	101	5	6.0	0.82
CV%	2.5	45	45		28		28	13
B/C 50-55 cm	4.84	0.6	2.5		35		1.9	1.01
CV%	1.4	20	30		28		32	10

filtration through a 00H-filter (Munktell analytical filter papers), until no traces of Cl^- were indicated by AgNO_3 dissolved in 10 ml water. The H^+ -saturated samples were titrated with NaOH . Duplicates corresponding to 0.7 g dry mass were suspended in 30 ml of 0.01 M CaCl_2 with 0, 1.92, 3.84, 5.75, 7.67 and 11.5 mmol L^{-1} NaOH . The $\text{pH}_{\text{CaCl}_2}$ was measured in the suspensions after 10 h of shaking followed by one hour of sedimentation.

The influence of ionic strength on the pH of "Al-rich" and "Al-poor" samples

The two samples with the largest amounts of Al_e from 2-3 cm depth in plot B, were mixed to form an "Al-rich" sample ($\text{Al}_e = 7.5 \text{ cmol kg}^{-1}$), and the samples with the smallest amounts were used to form an "Al-poor" mixed sample ($\text{Al}_e = 0.6 \text{ cmol kg}^{-1}$). Ten replicates of each of these two mixed samples, each corresponding to 1.0 g dry soil, were suspended in 25 ml distilled water and shaken for three hours. The pH was measured after one hour of sedimentation. The "Al-rich" suspensions were titrated down to the pH-value of the "Al-poor" ones, by adding a few droplets of HCl , whereupon 5.0 ml of KCl at each of five different concentrations (0.6, 0.03, 0.06, 0.003 and 0.006 M KCl) was added to the suspensions, giving five duplicates for each of the mixed samples. The pH_{KCl} was measured after three hours of shaking and one hour of sedimentation.

Results and discussion

Depth-related variation in pH_e , H_e and Al_e

Loss on ignition (LOI) was clearly related positively to both H_e and Al_e in the soil profile as a whole (Fig. 1), owing to an increase in the number of cation exchange sites with increasing LOI in the mineral soil. In the mor layer Al_e increased continuously with depth until the point at which the organic matter content dropped drastically, in the E-horizon. The exchangeable hydrogen ions (H_e), on the other hand, showed a maximum already at 2-3 cm depth, approximately at the boundary between the F- and H-horizons. The contribution of Al_e to the CEC_e relative to that of H_e , increased with depth in the humus layer. The pH_e -value (not shown) was negatively correlated ($p < 0.001$) with H_e in all cm-layers and decreased between 0-1 cm (3.52) and 2-3 cm (3.32), before increasing to a value of 3.42 at 4-5 cm depth. This paper focuses mainly on the relationship between pH and Al in the

TABLE III
SIMPLE LINEAR CORRELATION COEFFICIENTS (R) BETWEEN $\text{pH}_{\text{CaCl}_2}$ AND EXTRACTABLE POOLS OF Al AND Fe AS WELL AS BETWEEN $\text{pH}_{\text{H}_2\text{O}}$ AND POOLS OF Al AND Fe, IN THE MOR LAYER. THE INDEX DM DESIGNATES CORRELATIONS WITH VARIABLES EXPRESSED AS cmol kg^{-1} DRY MASS WHEREAS LOI DESIGNATES THE UNIT $\text{cmol kg}^{-1} \text{loi}^{-1}$. THE pH-VALUES WERE CORRECTED FOR LOI BY APPLYING SPECIFIC FUNCTIONS FOR EACH cm-LAYER AND ASSUMING THAT THE HYDROGEN IONS IN THE MOR LAYER ARE BOUND TO ORGANIC CATION EXCHANGE SITES, ACCORDING TO SKYLLBERG (1993). CORES WERE TAKEN FROM PLOT B. THE P DESIGNATES THE R-VALUE FOR SIGNIFICANCE AT THE 99% LEVEL.

		pH_e vs.			pH_H vs.			p	n
		$\lg \text{Al}_e$	$\lg \text{Al}_{\text{C}_{11}}$	$\lg \text{Fe}_{\text{C}_{11}}$	$\lg \text{Al}_e$	$\lg \text{Al}_{\text{C}_{11}}$	$\lg \text{Fe}_{\text{C}_{11}}$		
DM 0-1 cm		0.07	0.31	0.40	0.08	0.28	0.30	0.68	12
	LOI	0.07	0.31	0.39	0.08	0.27	0.29	0.68	12
DM 1-2 cm		0.39	0.66	0.74	0.43	0.70	0.76	0.66	13
	LOI	0.38	0.65	0.73	0.43	0.69	0.75	0.66	13
DM 2-3 cm		0.79	0.84	0.83	0.81	0.81	0.73	0.66	13
	LOI	0.76	0.81	0.80	0.78	0.78	0.68	0.66	13
DM 3-4 cm		0.83	0.73	0.69	0.84	0.58	0.44	0.71	11
	LOI	0.87	0.84	0.81	0.91	0.79	0.65	0.71	11
DM 4-5 cm		0.48	0.43	0.59	0.39	0.30	0.56	0.80	8
	LOI	0.85	0.92	0.93	0.92	0.88	0.90	0.80	8

TABLE IV

Table 4. Calculated $\text{pK}_a^{\text{app}}(\text{CEC}_e)$ and sample size adjusted coefficients of determination (r^2) for equations (1) and (2) with pH measured in 0.01 M CaCl_2 and in distilled water. The samples were taken from plot B. Samples taken at 2-4 cm were divided into two populations that differed in their amounts of CEC_e/LOI : S1 with 39.4 to 45.6 cmol kg^{-1} and S2 with 47.4 to 56.5 cmol kg^{-1} .

Humus cm-layer	n	$\text{pH}_{\text{CaCl}_2}$			$\text{pH}_{\text{H}_2\text{O}}$		
		Eq. (1) r^2	Eq. (2) pK_a^{app}	r^2	Eq. (1) r^2	Eq. (2) pK_a^{app}	r^2
0-1	12	(0.68)	2.86	(0.78)	(0.63)	3.54	(0.71)
1-2	13	(0.62)	2.89	(0.88)	(0.58)	3.72	(0.87)
2-3	12	(0.05)	2.85	(0.74)	(0.03)	3.80	(0.62)
3-5	18	-(0.14)	2.89	(0.55)	-(0.23)	3.81	(0.49)
2-4 S1	13		2.86	(0.94)		3.75	(0.76)
2-4 S2	12		2.72	(0.90)		3.68	(0.61)

Note that Table 4 is corrected for printing errors

lower part of the mor layer, stippled in Figure 1.

The amount of Al_e was positively correlated between all cm-layers of a humus core ($p < 0.001$, $p < 0.01$ between 0-1 and 4-5 cm) and the mean Al_e -value of the mor layer was positively correlated ($p < 0.001$) to each of the uppermost two centimeters of the E-horizon. This means that the spatial variation showed a similar pattern at all depths in the mor layer and in the upper part of the E-horizon. Such correlations were not as strong for H_e , but pH_e was positively correlated ($p < 0.001$) between the O- (0-5 cm) and the E-horizons (0-5 cm).

Spatial variation did not differ significantly among the plots, despite their different sizes. Calculated semi-variances suggested that auto-correlations within the range 0.5 to 10 m were small in all cm-layers or horizons. As a consequence of the relatively large, but uniform, variation the humus cores were regarded as being independent of each other and could be statistically treated as belonging to the same sample population.

Correlations between pH_e and pools of extractable aluminum

The negative correlations between pH_e and Al_e in the B- and B/C-horizons (Figure 2) could be explained by an increase in the solubilization of aluminum hydroxides with decreasing pH. The exchangeable Al pool is, however, much larger than Al in solution, and is dependent on the availability of cation exchange sites. Therefore the relationship between pH_e and Al_e is affected by an indirect component related to the variation in CEC_e .

The positive correlation ($p < 0.001$) between pH_e and Al_e in the mor layer (Figure 2) has not been reported before. One reason for this could be the lack of small-scale studies of organic horizons with relatively uniform CEC_e -values among samples. With a substantial variation in CEC_e the cation exchange processes would be obscured by an overall positive correlation between the amount of cations and the number of cation exchange sites. Tamminen and Starr (1990) reported a negative correlation between pH_{H_2O} and Al extracted in 0.1 M $BaCl_2$ from 65, mainly Podzols, humus layers in southern Finland. Looking at their results and restricting the samples to humus layers with a pH_{H_2O} below 4.5 there was no relationship between pH_{H_2O} and Al.

Figure 3 furthermore illustrates the pH/Al -relationship. The sub-population with small amounts of Al_e

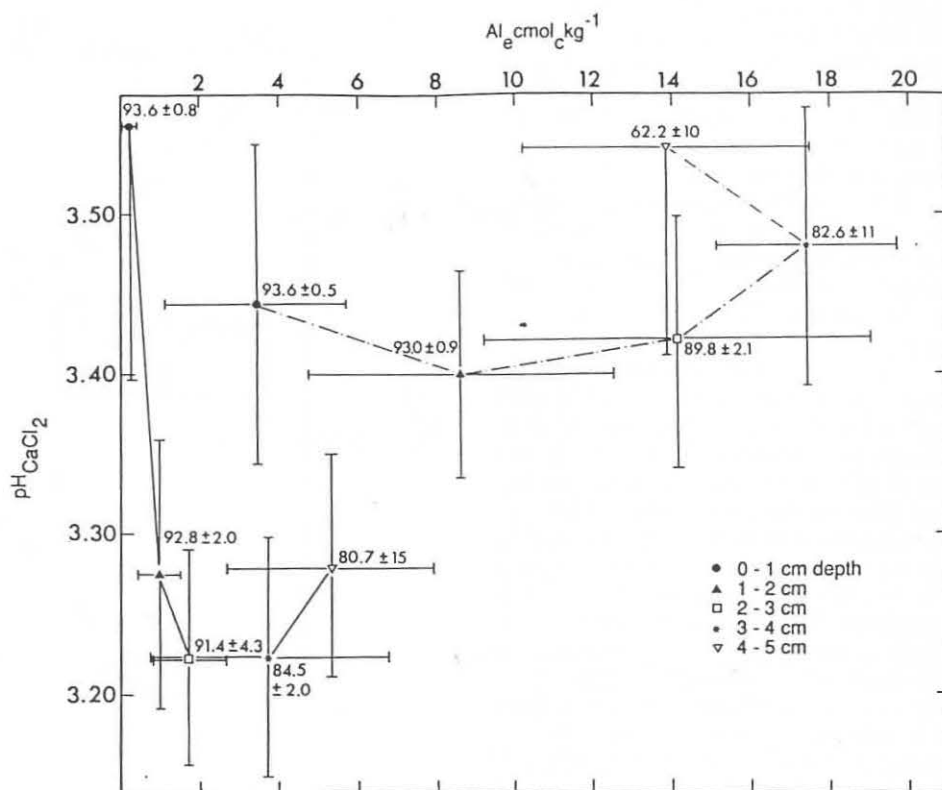


Figure 3. Mean pH_e and Al_e values for two subpopulations of mor samples from plot A. The dotted line represents a subpopulation of cores with Al_e more than 3.0 cmol_c kg⁻¹ at 1-2 cm ($n=6$), whereas the other sub-populations had lower amounts of Al_e ($n=4-6$). Loss on ignition + CV% is given for each depth. The bars illustrate the 95-% confidence intervals for pH_e and Al_e .

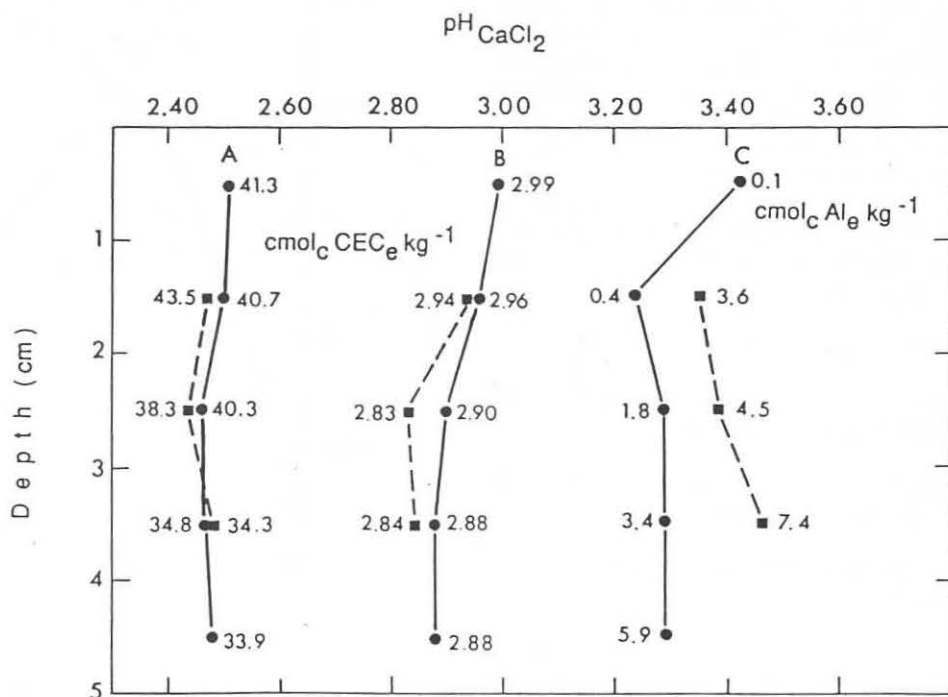


Figure 4. Mixed humus samples from the cm-layers of plot B. Broken and solid lines represent relatively Al_e -rich and Al_e -poor samples, respectively. A: pH measured in 0.01 M $CaCl_2$ for H^+ -saturated samples, with amounts of CEC_e noted for each sample. B: The acid strength of the H^+ -saturated samples, expressed as pH_e at neutralization of 1/2 CEC_e , with the $pK_{a^{app}}(CEC_e)$ -values noted. C: Mean pH_{CaCl_2} for individual, natural samples, with amounts of Al_e noted.

showed a pH_c -gradient typical for most studied mor layers, with pH being significantly higher in the upper part (F-layer) than in the lower part (H-layer; Hesselman, 1926; Mattson and Koutler-Andersson, 1941; Skjellberg, 1990). By contrast, the "Al-rich" cores did not show any depth-gradient at all. At 2-3 cm depth, and below, LOI was lower in the "Al-rich" cores than in the "Al-poor" cores but, as pointed out earlier, no significant correlation ($-0.1 < r < 0.1$) was found between LOI and Al_c in any cm-layer.

The proportion of the total organic pool of Al (Al_{Cu} ; Hargrove and Thomas, 1984) that was KCl-exchangeable increased from 26% at 0-1 cm to 61% at 4-5 cm. The linear regression between these pools showed that Al_c reflected the total amount of Al bound in the mor layer ($\text{Al}_{\text{Cu}} = -0.3035 + 1.6338 \text{ Al}_c$, $r^2=0.91$; 0-5 cm; $n=57$). This was in agreement with Nättscher (1987) who found a strong relationship between Al extracted in 0.33 M CuCl_2 and in 1.0 M NH_4Cl in L- and O-horizons. The correlation between Al_{Cu} and Fe_{Cu} was also very strong ($r^2=0.82$; 0-5 cm; $n=57$). Table III shows that all of the measured Al- and Fe-pools were similarly correlated to both pH_c and pH_{in} .

A stronger relationship was found between pH and pools of Al and Fe when the variation in organic matter content was excluded by expressing the variables in relation to the loss on ignition. This was evident at 3-5 cm depth where the variation of LOI was relatively large. These relationships indicate some type of competition between Al (and Fe) and H for organic cation exchange sites as an important pH -buffering process in the mor layer.

The role of exchangeable Al for pH -buffering in the mor layer in relation to the effective cation exchange capacity

The pH -value in a humus sample is a function of:

- (1) the acid strength (pK_a^{app}) of the buffering organic acids/bases
- (2) the amount of the buffering acids/bases (cmol CEC kg^{-1})
- (3) the protonation of the buffering acids/bases

To determine whether the positive relationship between pH and Al_c was a direct one, caused by an active pH -buffering of Al compounds, or an indirect one caused by covariation with some of the factors (1), (2) or

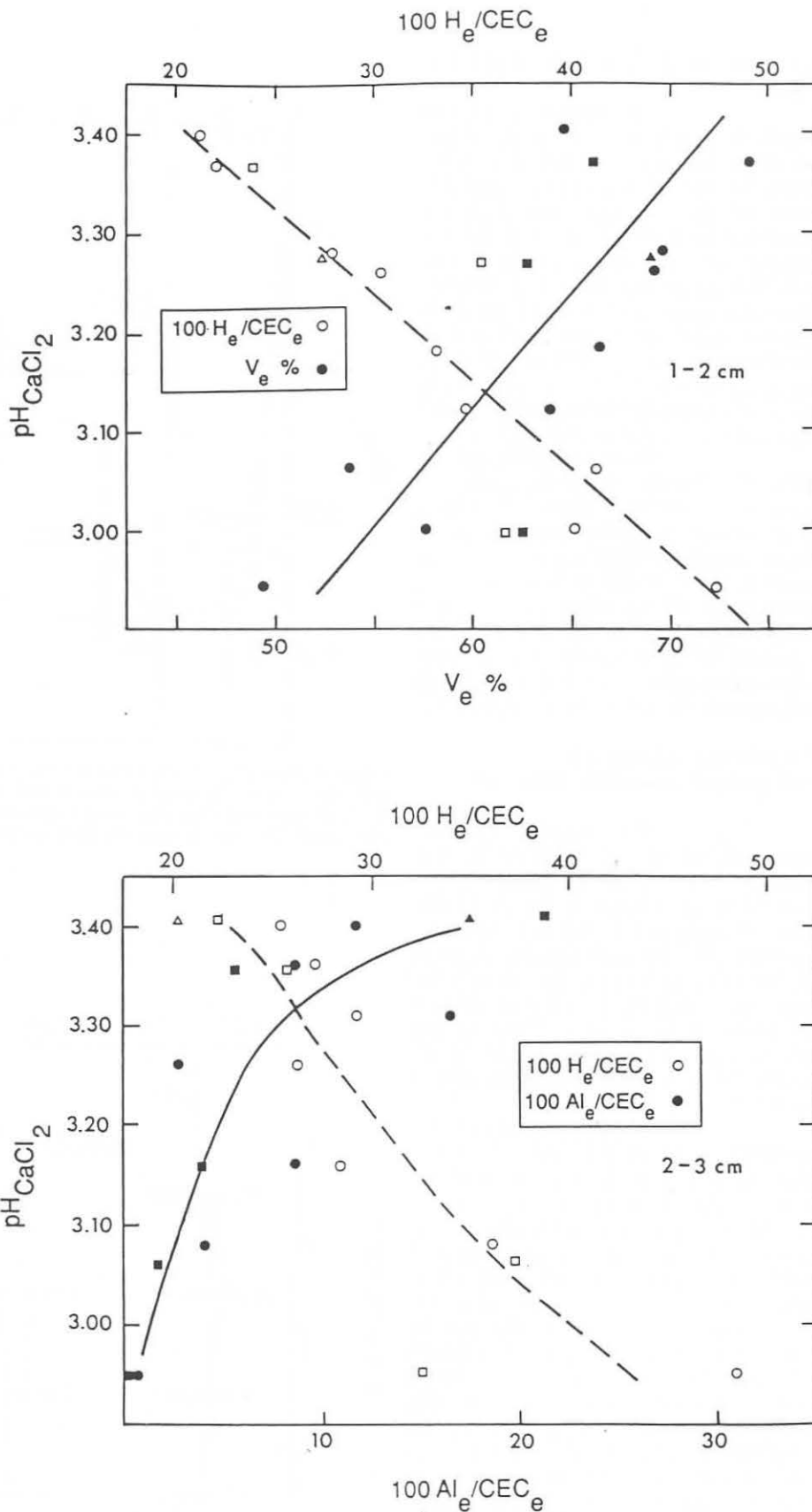


Figure 5. Relationships between pH_c and effective base saturation (V_e %), pH_c and aluminum saturation of cation exchange sites (Al_c/CEC_e) and between pH_c and the protonation of cation exchange sites (H_e/CEC_e) at 1-2 and 2-3 cm depth in the humus layer of plot B.

3) these factors were examined in samples from plot B with different amounts of Al_e .

The acid strength (1) was estimated for H^+ -saturated samples in section i). In section ii) the degree of protonation of the exchange sites (3) was calculated as the amount of protons in relation to the amount of organic acids (CEC_e), with and without the inclusion of protons bound to Al -ions. In section iii) the inability of Al bound to organic matter to release protons (hydrolyze) was shown in a laboratory experiment.

i) Estimation of the acid strength of the humus samples

The pH-dependent charges of organic matter are often regarded as a mixture of weak acid functional groups with overlapping pK_a -values that can be described in terms of a mean apparent acid strength (pK_a^{app} , e.g. Stevenson, 1982). Although titration curves of solid phase humus often are practically linear and do not show any distinct inflection points (Hargrove and Thomas, 1982; Federer and Hornbeck, 1985; Nättscher and Schwertmann, 1991), the CEC at pH 7.0 or 8.2 has been used to estimate the amount of negative charges at complete dissociation of the organic acids (e.g. Bloom and Grigal, 1985; Walker *et al.*, 1990).

In this study the acid strength of the organic acids was estimated for mixed humus samples from plot B by titration of H^+ -saturated samples with NaOH in 0.03 M ionic-strength medium (see Material and methods). The titration curves for the humus one-cm-layers were closely parallel to each other in the pH_e interval from 2.5 to 5.0 and did not show any distinct inflection points up to pH_e 7.0 (data not shown). To examine whether the pH/Al_e relationship was caused by covariation with the acid strength, the negative charges included in the CEC_e were assumed to be more relevant for the pH-buffering in the pH_e -interval from 2.5 to 4.0 than were functional groups contributing with negative charges at higher pH. Therefore CEC_e was chosen as an estimation of the amount of organic acids/bases to be used when determining the acid strength $pK_a^{app}(CEC_e)$.

The $pK_a^{app}(CEC_e)$ -values were measured as the pH_e with half of the CEC_e neutralized (Figure 4). The 0-1 cm showed a slightly higher $pK_a^{app}(CEC_e)$ than the other cm-layers otherwise there were small differences in acid strength among the cm-layers and among samples with different amounts of Al_e . Because variation in CEC_e was low the relations

Note that Table 5 is corrected for printing errors

TABLE V

EXCHANGEABLE CATIONS IN TWO MIXED SAMPLES FROM 2-3 CM DEPTH IN PLOT B. EXCHANGEABLE ACIDITY (EA) REPRESENTS THE SUM OF H_e AND Al_e .

	Al_e	H_e	EA	Ca+Mg+ Mn+Na+K	CEC_e	$V_e\%$
Mixed sample	----- $cmol_e kg^{-1}$ -----					
"Al-rich"	8.2	8.9	17.1	24.8	41.9	59
"Al-poor"	1.0	16.4	17.4	25.4	42.8	59

among the $pK_a^{app}(CEC_e)$ values from different depths were in good agreement with the relations among pH_e -values at H^+ -saturation. In an estimation of pK_a^{app} , with pH 4.0 and 5.0 chosen as reference-pH values for complete dissociation of the organic acids, the acid strength relations obtained among samples were similar to those obtained for $pK_a^{app}(CEC_e)$.

The results suggest that pH-differences among samples with different amounts of Al_e were not caused by a covariation with the amounts of organic acids (CEC_e) or the acid strength of the acids/bases.

ii) The relevance of considering Al_e as a neutralizing cation or as an acidic cation contributing to the protonation of CEC_e

The effective cation exchange capacity was positively correlated with the sum of the cations $Ca+Mg+K+Na$ ($cmol_e kg^{-1}$, $p<0.001$ below 1-2 cm) and with H_e ($p<0.01$ below 2-3 cm) at all depths. Exchangeable Al and pH_e were not significantly correlated with CEC_e at any depth in the mor layer. It can be assumed that amounts of $Ca+Mg+K+Na$ and H_e are more closely related to decomposition and humification processes than is the Al_e , which is derived mainly from the mineral soil, independently of these processes. To exclude the influence of variation in CEC_e among samples, variables were expressed in relation to CEC_e .

The effective base saturation is the percentage of the CEC_e that is balanced by neutralizing nonacidic cations $V_e\% = 100(Ca+Mg+K+Na)/CEC_e$. The base saturation is inversely related to the degree of protonation, with Al_e included as three protonated charges ($V_e = 1-(H_e+Al_e)/CEC_e$). In this study $V_e\%$ was

relevant in describing the buffering of pH_e only at 0-1 and 1-2cm (Figure 5). Further down in the mor layer substantial amounts of Al_e were present and the relation between pH_e and $V_e\%$ weakened and eventually turned negative at 3-4 cm ($p<0.01$). If Al_e , on the other hand, was included as a nonacidic cation, the H_e/CEC_e quotient ($=1-(Al+Ca+Mg+K+Na)/CEC_e$) accurately described the pH-buffering by cation exchange in all cm-layers (Figure 5). The important role of Al_e as a neutralizing cation in this quotient was shown by the positive relationship between Al_e/CEC_e and pH_e below 1-2 cm (Figure 5).

The extended Henderson-Hasselbach equation

$$pH = pK_a^{app} + n \log(V_e/(1-V_e)) \quad (1)$$

has been used to describe the pH-buffering by cation exchange in soils on a thermodynamical basis (Bloom and Grigal, 1985). The pK_a^{app} is the apparent acid strength, n is an empirical constant and V_e the base saturation at pH 7.0, with exchangeable Al included with three charges (equivalent to protons) in the denominator ($cmol_e (Ca+Mg+K+Na)/(H+Al)$).

In this study equation (1) was modified and based on CEC_e instead of $CEC_{pH 7.0}$ (by changing V_e to V_e). To evaluate the degree to which Al_e contributed to the protonation of the organic acids at natural pH-values in the mor layer, equation (1) was compared to equation (2), in which Al_e was included as a neutralizing cation considered not to hydrolyze.

$$pH = pK_a^{app}(CEC_e) + n \log((Ca+Mg+K+Na+Al_e)/H_e) \quad (2)$$

Table IV lists the coefficients of determination (r^2) for the regressions between exchangeable cations and pH. Equation (1) was only relevant for describing the pH-buffering in the uppermost two cm-layers, where Al_e was of minor importance. Equation (2) was, however, superior to equation (1) at all depths, both in 0.01 M $CaCl_2$ and in H_2O . The intercept ($pK_a^{app}(CEC_e)$) showed relatively small differences among the cm-layers.

This was in accordance with the laboratory estimations (Figure 4). The equations could only be used properly on a uniform population of samples of similar acid strength. Therefore populations were restricted to samples within a specified cm-layer.

To get even more uniform populations, with a restricted amount of organic acids/bases, the samples from 2-3 and 3-4 cm depth were classified according to amount of CEC_e/LOI (S1 and S2, Table IV). As much as 95% ($r^2=0.95$) and 91% of the variation of pH_e was accounted for by equation (2) when Al_e was included as a nonhydrolyzed neutralizing cation (Al^{3+}) in S1 and S2 (equation 2). When Al_e was assumed to be slightly hydrolyzed and bound as $Al(OH)_{1/6}^{2.5+}$ to the organic acids r^2 decreased slightly in both S1 and S2, indicating that Al_e was acting as a neutralizing cation with no substantial degree of hydrolyzation.

iii) The influence of ionic strength on the pH of humus samples differing in the amounts of exchangeable Al

Figure 6 illustrates the effect of ionic strength on the pH-value of two samples differing in Al_e content. The samples were taken at 2-3 cm depth in the mor layer from plot B and had very similar contents of CEC_e , EA and V% (Table V). Since no substantial differences were found in the acid strength (see section i), the distribution of exchangeable acidity into Al_e and H_e was the only difference between samples.

The Al-poor sample released about twice as much H^+ into solution (0.3 pH-units) compared with the Al-rich one, at all levels of ionic strength. This was in agreement with the relative amounts of H_e in the untreated samples (Table V) and indicated that there was no substantial release of protons owing to hydrolyzation of organically bound Al_e .

Exchangeable acidity ($H_e + Al_e$) showed relatively low spatial variation at all depths (CV% 13-15% from 0-1 to 3-4 cm and 31% at 4-5 cm in plot

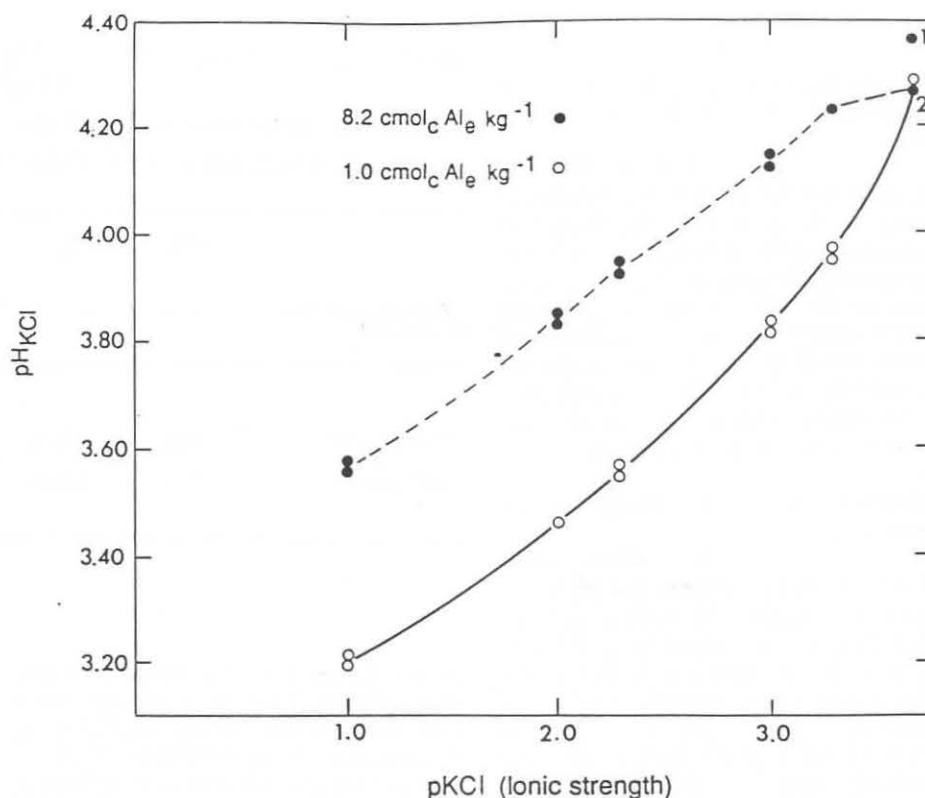


Figure 6. The pH_{KCl} in two humus samples whose properties are described in Table V. The Al-rich samples were titrated down from 4.37 (1) to 4.27 (2) before the ionic strength was increased with KCl to 0.0005, 0.001, 0.005, 0.01 and 0.1 M.

B), indicating that the input and/or production of acidity were spatially rather uniform in the mor layer. The relative contributions of Al_e and H_e to the acidity showed a much larger spatial variation and were decisive for the realization of exchangeable acidity into hydrogen ions in solution. Thus it can be concluded that the difference in pH between samples mainly was due to whether the protons were bound directly to cation exchange sites or bound stronger in aluminum ions. **Sources and reactions of aluminum in the humus layer - theory**

In sections i) to iii) it was shown that the positive correlation between pH and Al_e was not caused by variation in acid strength or in the amount of organic acids. Exchangeable Al did not hydrolyze substantially, thus it behaved like a nonacidic cation in the mor layer. These findings, however, do not explain the processes involved in the competitive interaction between H and Al

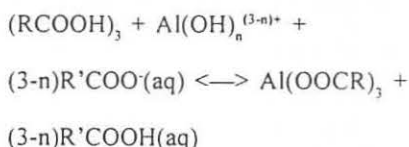
in the lower part of the mor layer.

The main source of protons in humus layers in areas receiving little atmospheric acid deposition is the uptake of nutrient cations by roots, leading to a successive protonation of CEC_e . In combination with an increasing CEC_e and a decreasing pK_a^{app} of the organic matter during the initial stages of decomposition (i.e. 0-1 to 1-2 cm in Fig. 4), this gives rise to a pH decrease with depth in the upper part of the mor layer (Skjellberg, 1990; and Figure 3). With increasing depth, however, silicate weathering can be assumed to increase its contribution to the acid/base status.

If root uptake is effective, the consumption of protons associated with the release of nutrient cations from silicates is balanced by an equivalent release of protons. Aluminum- and Fe-cations are, however, not taken up and bind strongly to exchange sites of organic matter (and root surfaces). Aluminum and Fe can be assumed to accu-

multate in the lower part of the O-horizon, balancing CEC negative charges in an equivalent amount to protons consumed upon weathering of $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$. Although the degree of Al_c hydrolyzation in this study appeared to be insignificant, substantial hydrolyzation has been reported in peat soils even at pH-values below 4.0 (Hargrove and Thomas, 1982). The number of protons that will be consumed, or leached, from the humus layer, for each bound monomer aluminum cation varies depending on whether or not the neutralization of $\text{Al}(\text{OH})_3$ is coupled to a direct H/Al cation exchange on soil organic matter and on the degree of hydrolyzation of bound aluminum.

Schematically, positively charged Al-species ($\text{Al}(\text{OH})_n^{(3-n)+}$), which can be supposed to be balanced by organic anions in solution ($\text{R}'\text{COO}^-(\text{aq})$), may neutralize or exchange protons bound to cation exchange sites (RCOOH):



The reaction is promoted by the presence of protonated organic exchange sites with relatively low pK_a -values, which can donate protons to the hydrolyzed Al-species and/or to the dissolved organic anion balancing Al in solution. For every bound $\text{Al}(\text{OH})_n^{(3-n)+}$, n protons are neutralized by Al and $3-n$ protons are exchanged into solution. Although some hydrolyzation may take place the pH will rise because the acid strength of the Al-organic matter is lower than that of the H-organic matter (Hargrove and Thomas, 1981, 1982; Nätscher and Schwertmann, 1991).

In situations where the acid strength of the dissolved organic acid $\text{R}'\text{COOH}(\text{aq})$ is lower than that of the solid phase carboxylic groups RCOOH , the exchange reaction above will be shifted to the right. The exchanged protons will be more tightly bound and pH will increase. Through this mechanism a simple exchange of 3H^+ for Al^{3+} can give rise to a pH-increase. Since dissolved aluminum exists predominately in the form of organic complexes in mor layers (e.g. David and Driscoll, 1984; Giesler and Lundström, 1990), competition between soluble organic anions and solid-phase negative charges for aluminum and hydrogen ions could be involved in the pH/Al interaction.

The increase of accumu-

lated Al with depth in the mor layer (Figure 2 and 3) in combination with a significant ($p < 0.001$) positive correlation between Al_c in the mor layer and Al_c in the eluvial horizon, suggests that soluble Al is either transported upwards from the mineral soil, or that Al accumulates in, or in association to, roots and is subsequently incorporated into relatively resistant humus compounds during decomposition. Because of the weak relation between LOI and Al-pools, the absolute amount of mineral particles in the mor layer does not seem to be of significance for the amount of accumulated Al. Even small amounts of mineral particles could probably release large amounts of Al depending on mineral composition, the quality of the organic acids and time of exposure. A subjective examination of the cores from plot B with the naked eye indicated that cores with a more well developed H-layer, i.e. black with a greasy consistency, had larger amounts of Al_c and Al_{co} than did cores with more finely structured H-layers. The massive weak structure may reflect more wet conditions, older, more decomposed humus or humus derived from a slightly different substrate (Klinka *et al.* 1981).

Cycling of Al-species by vegetation varies in magnitude between coniferous ecosystems. Vogt *et al.* (1987) found that of the total amount of cycled Al in an *Abies amabilis* stand, 97% was cycled through the roots. Aboveground cycling would probably not result in the large degree of spatial variation in Al_c found in this study. Transport of Al from the mineral soil to the humus layer could also be mediated by fungi.

Conclusions

Exchangeable aluminum was ineffective in releasing protons upon hydrolyzation in the naturally acid mor layer with a pH in 0.01M CaCl_2 around 3.40. The lack of substantial hydrolyzation gave Al^{3+} properties more like a nonacidic cation, which was shown by an extended Henderson-Hasselbach equation. The equation best fit the data when Al_c was included with three charges as a neutralizing, nonacidic cation:

$$\begin{aligned} \text{pH} &= \text{pK}_a^{\text{app}}(\text{CEC}_c) + \\ &\text{nlog}(\text{Ca}+\text{Mg}+\text{K}+\text{Na}+\text{Al}_c)/\text{H}_c \end{aligned}$$

The pH-value in the mor layer was mainly buffered by cation exchange, with aluminum being the most important of the neutralizing cations balancing dissociated organic acids. The

sources of Al and processes behind the competitive interaction between H and Al for cation exchange sites remain to be further determined.

In any analysis of exchangeable acidity in naturally acid organic horizons, one should distinguish between protons bound to organic exchange sites and those derived from aluminum.

The usefulness of a small-scale sampling design for studies of soil chemical processes in natural samples was shown.

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